

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-270238  
(43)Date of publication of application : 02.10.2001

(51)Int.CI. B41M 5/00  
B41J 2/01

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(30)Priority  
Priority number : 2000007755 Priority date : 17.01.2000 Priority country : JP

## (54) INK JET RECORDING MEDIUM

**(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide an ink jet recording medium having excellent recording suitability by not only a dye ink but also a pigment ink and particularly excellent water resistance as storage stability by recording a highly minute image with good reproducibility.

**SOLUTION:** The ink jet recording medium comprises an ink acceptive layer containing at least one type of the pigment selected from the group consisting of minerals having a mean particle size of 2 to 17  $\mu\text{m}$ , an amorphous silica, alumina, alumina hydrate, aluminosilicate and hydrotalcite and an adhesive on a support. In this case, the adhesive contains a vinyl chloride-vinyl acetate copolymer.

## **LEGAL STATUS**

[Date of request for examination]  
[Date of sending the examiner's decision of rejection]  
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]  
[Date of final disposal for application]  
[Patent number]  
[Date of registration]  
[Number of appeal against examiner's

[decision of rejection]

[Date of requesting appeal against  
examiner's decision of rejection]

[Date of extinction of right]

## CLAIMS

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[Claim(s)]

[Claim 1] The ink jet record medium which is an ink jet record medium which mean particle diameter is 2-17 micrometers, and comes to prepare the ink absorbing layer containing at least one sort of pigments chosen from amorphous silica, an alumina, hydrated alumina, aluminosilicate, and a hydrotalcite group mineral, and adhesives on a base material, and is characterized by said adhesives containing a vinyl chloride vinyl acetate copolymer.

[Claim 2] The ink jet record medium according to claim 1 whose loadings of the vinyl chloride vinyl acetate copolymer in an ink absorbing layer are 5 - 50 weight section to the pigment 100 weight section.

[Claim 3] The ink jet record medium according to claim 1 or 2 with which an ink absorbing layer contains cation resin further.

[Claim 4] The ink jet record medium according to claim 1 to 3 which the oil absorption to which at least one sort of pigments chosen from amorphous silica, an alumina, hydrated alumina, aluminosilicate, and a hydrotalcite group mineral apply to JISK5101 is 300ml / 100g or more, and contains this pigment ten to 50% of the weight to all the pigment solid content in an ink absorbing layer.

[Claim 5] It is the ink jet record medium according to claim 1 to 4 whose pigment chosen from amorphous silica, an alumina, hydrated alumina, aluminosilicate, and a hydrotalcite group mineral is amorphous silica, these whose amorphous silica is two or more sorts of concomitant use and whose difference of the secondary particle mean particle diameter of at least two sorts of amorphous silica is 2-7 micrometers.

[Claim 6] The ink jet record medium according to claim 3 whose cation resin is the copolymerization object of a polydiallyldimethylammonium salt and acrylamide.

[Claim 7] The ink jet record medium according to claim 1 to 6 which prepared the binder layer and the exfoliation sheet in the base material rear face.

[Claim 8] The ink jet record medium according to claim 1 to 7 which gives the drop of the ink which contains a pigment as a coloring agent, and acquires record.

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the record medium for ink jets which was excellent in ink absorptivity and the repeatability of an image, and was especially excellent in shelf lives, such as a water resisting property, about the ink jet record medium which uses and records oily ink or water color ink on a record medium.

[0002]

[Description of the Prior Art] Application to a printer for terminals, facsimile, a plotter,

or document printing from the reasons that the ink jet recording method using water color ink has little noise at the time of record, and colorization is easy, nil why high-speed record is possible, etc. is advanced. Since the long duration remainder, equipment, and the sheet printed continuously are polluted, without the printed ink drying on a paper front face since the absorptivity of ink is inferior or an image becomes dirty, the paper of fine quality and coated paper which are used for general printing are lacking in practicality. In order to solve such a problem, the record medium which infiltrated the water soluble polymer into what the low recording paper of whenever [ size ] is used for (JP,52-53012,A), and the stencil paper which carried out internal [ of the urea-formalin resin ] is indicated (JP,53-49113,A). Furthermore, the record form (JP,55-51583,A, JP,56-148585,A) which applied various porosity inorganic pigments including amorphous silica to the front face in order to raise the color enhancement of ink and repeatability is indicated. Moreover, amelioration of specifying the physical properties of these porosity pigments in order to obtain the high definition image which suppressed the blot is proposed (JP,58-110287,A, JP,59-185690,A, JP,61-141584,A).

[0003] As an example which uses an organic pigment, the coating sheet for ink jet record of the coating layer containing an oil absorption nature inorganic pigment, an organic pigment, and drainage system adhesives (JP,64-24785,A) is indicated. However, it was only having oily ink jet record fitness, and was not what combines aquosity ink jet record fitness and oily ink jet record fitness. Although the recorded body (JP,57-82085,A) which the polystyrene particle was added, and absorption of ink controlled the diffusion to the longitudinal direction of ink early, and raised resolution was indicated, this was also inferior to surface reinforcement and there was a fault which paper powder produces.

[0004] Color ink is a subject, the ink for ink jets currently used from the former oxidized by ultraviolet rays, ozone, etc. in the long-term notice, and the image faded and it had the problem that appearance got worse. In order to solve such a problem, using the pigment ink which was excellent in lightfastness compared with color ink is indicated by JP,9-157559,A, JP,9-132740,A, etc. However, although colored by things, since [ color ink "dyes" an acceptance layer by the low molecular weight compound ] pigment ink is coloring the pigment particle by "it covering" or the thing "put in order" on the acceptance layer, the properties for which a record object is asked differ. Moreover, compared with a color, molecular weight of a pigment is very large, therefore the present condition is that the reactions of the low-molecular level of a color completely differ, and property sufficient in respect of printing concentration, a blot, etc. with the conventional sheet for record is not acquired for fusers, such as control of a blot,, either. Especially in the label application which formed the binder layer and the releasing paper in the rear face, since the shelf life of a record part is required, the record medium corresponding to pigment ink is demanded.

[0005] However, compared with the method which used color ink, record concentration cannot come out of this method using pigment ink easily. Conversely, in order to take out record concentration, when it left ink to the record-medium front face, the record image front face was worn, it was alike, and there was a fault that an image became thin more or natural complexion became dirty. Moreover, when water was poured on a record image front face, there was a fault in which ink oozes out and to which the so-called water resisting property worsens. These problems are faults produced since pigment ink was not enough established on recorded media, and it was not able to solve in the

conventional recorded media only supposing what is recorded in color ink.

[0006] About the water resisting property of printing, in using disperse dye type ink, if the device of a printer becomes complicated by the method which applies a deck-watertight-luminaire-ized agent before and after printing as shown in JP,9-188062,A etc., and liquid absorption capacity of a record medium is not made [ many ], a blot of printing which is called the so-called bleeding will occur. According to this method, the maintenance of a deck-watertight-luminaire-ized agent was needed with ink, and there were problems, like a running cost goes up.

[0007] Thus, the requests which adopt pigment ink are mounting on industrial ways whose shelf lives of a record part are conditions absolutely, such as an ink jet label paper. It is called for that a pigment ink type is fixed to a record-medium front face at the point which ink reached on the surface of the record medium as the description. Paying attention to generally the dispersing element of pigment ink being anionic as a device of fixing, the method which makes an ink absorbing layer contain a cationic component, and makes it condense is taken. Although a lot of cation components were required for fixing of the color by the color ink type, in order for condensation in a front face to become it strong that a cation component is superfluous too much, and for distribution of ink to serve as an ununiformity and to cause the fall of record concentration, the record excellent in the case where the conventional record medium corresponding to color ink is diverted as it was was not acquired by the pigment ink type.

[0008]

[Problem(s) to be Solved by the Invention] In color ink, since the color molecule is very small, in case it moves with a solvent, a color is combined and colored an acceptance layer. Therefore, although it was in the inclination whose printing concentration improves when the absorption capacity of an acceptance layer was low, in pigment ink, such a phenomenon did not happen at all. That is, the coloring device of color ink of the coloring device of pigment ink was what is completely different. In the record approach using pigment ink, it is the property further needed for the ink jet record medium for pigment ink making a pigment component exist in homogeneity at the acceptance layer surface section by the ability of a pigment particle raising printing concentration to homogeneity by "it arranging" or the thing "with which it covers" at the acceptance layer surface section, and absorbing the solvent of ink promptly inside an acceptance layer.

[0009] This invention improves the above-mentioned fault, is excellent not only in color ink but the record fitness in pigment ink, can record a high definition image with good repeatability, and offers the waterproof outstanding record medium for ink jets especially as shelf life.

[0010]

[Means for Solving the Problem] This invention contains each following mode.

[1] The ink jet record medium which is an ink jet record medium which mean particle diameter is 2-17 micrometers, and comes to prepare the ink absorbing layer containing at least one sort of pigments chosen from amorphous silica, an alumina, hydrated alumina, aluminosilicate, and a hydrotalcite group mineral, and adhesives on a base material, and is characterized by said adhesives containing a vinyl chloride vinyl acetate copolymer.

[2] The ink jet record medium given in [1] the given loadings of the vinyl chloride vinyl acetate copolymer in an ink absorbing layer are 5 - 50 weight section to the pigment 100 weight section.

[3] [1] in which an ink absorbing layer contains cation resin further, or an ink jet record medium given in [2].

[0011] [4] At least one sort of pigments chosen from amorphous silica, an alumina, hydrated alumina, aluminosilicate, and a hydrotalcite group mineral are JIS. Ink jet record medium given in either of [1]- [3] which the oil absorption according to K5101 is 300ml / 100g or more, and contains this pigment ten to 50% of the weight to all the pigment solid content in an ink absorbing layer.

[5] It is an ink jet record medium given in either of [1]- [4] whose pigments chosen from amorphous silica, an alumina, hydrated alumina, aluminosilicate, and a hydrotalcite group mineral are amorphous silica, these whose amorphous silica is two or more sorts of concomitant use and whose differences of the secondary particle mean particle diameter of at least two sorts of amorphous silica are 2-7 micrometers.

[6] The ink jet record medium given in [3] given cation resin is the copolymerization object of a polydiallyldimethylammonium salt and acrylamide.

[0012] [7] An ink jet record medium given in either of [1]- [6] which prepared the binder layer and the exfoliation sheet in the base material rear face.

[8] An ink jet record medium given in either of [1]- [7] which gives the drop of the ink which contains a pigment as a coloring agent, and acquires record.

[0013] [9] An ink jet record medium given in either of [1]- [8] at least one sort of whose pigments chosen from amorphous silica, an alumina, hydrated alumina, aluminosilicate, and a hydrotalcite group mineral are amorphous silica.

[10] An ink jet record medium given in either of [1]- [9] in which the adhesives of an ink absorbing layer contain silanol denaturation polyvinyl alcohol further.

[0014]

[Embodiment of the Invention] About the ink jet record medium which uses and records oily ink or water color ink on a record medium, it excelled in ink absorptivity and the repeatability of an image especially, and this invention had surface reinforcement sufficient as an office form, and there was little generating of paper powder at the time of conveyance by the printer, and it found out that a problem was solvable by blending various \*\*\*\*\* results and a vinyl chloride vinyl acetate copolymer for examination of the record medium for ink jets which was excellent in the water resisting property especially as shelf life.

[0015] In order to have sufficient surface reinforcement as an ink jet record medium and to raise the water resisting property of a printing image, chemical resistance, dirt-proof, paint film reinforcement, abrasion resistance, and adhesion use at least the vinyl chloride vinyl acetate copolymer which is excellent compared with adhesives, such as various resin, such as acrylic resin, a vinyl chloride-ethylene copolymer, and urethane resin, and a copolymer, as some adhesives.

[0016] A vinyl chloride vinyl acetate copolymer is a copolymer which contains a vinyl chloride and vinyl acetate as a monomer presentation. Vinyl chloride-vinyl acetate copolymerization, a vinyl chloride-vinyl acetate-ethylene copolymer, a vinyl chloride-vinyl acetate-acrylic copolymer, a vinyl chloride-vinyl acetate-ethylene-acrylic copolymer, a vinyl chloride-vinyl acetate-acrylic-acid dihydroxy propyl copolymer, a vinyl chloride-vinyl acetate-acrylic-acid hydroxypropyl copolymer, etc. can be illustrated, and a copolymer with monomers other than a vinyl chloride and vinyl acetate (monomer component of the 3rd [ \*\* ] and 4th grade) is sufficient. Copolymerization of

the hydrophilic polymer can be further carried out to said copolymer. In addition, the copolymer mainly concerned with vinyl chloride-vinyl acetate may be used together with other adhesives in the range which does not check desired effectiveness.

[0017] The loadings of the copolymer mainly concerned with the vinyl chloride-vinyl acetate to an ink jet record medium have desirable 5 - 50 weight section to the pigment 100 weight section, and its range of 10 - 40 weight section is usually more desirable. In addition, especially weight % in the adhesives in the case of using together with other adhesives does not limit.

[0018] The adhesives of further others can be used together as adhesives. For example, starch and its derivative, a carboxymethyl cellulose, hydroxyethyl cellulose, Nature or semi-synthetic polymers, such as casein, gelatin, and soybean protein, Polyvinyl alcohol and its derivative, polyvinyl butyral resin, Polyethyleneimine system resin, polyvinyl-pyrrolidone system resin, Pori (meta) acrylic-acid system resin, Acrylic ester system resin, polyamide system resin, polyacrylamide system resin, Polyester resin, a urea-resin, urethane resin, melamine resin, a styrene-butadiene copolymer, Well-known ingredients, such as a water solution of vinyl system copolymer resin, such as a methyl-methacrylate-butadiene copolymer and an ethylene-vinylacetate copolymer, a water dispersing element, or a denaturation polymer that introduced anionic or cationic residue into the above-mentioned resin, can be used suitably. Especially, since surface reinforcement is excellent, especially concomitant use of silanol denaturation polyvinyl alcohol is desirable.

[0019] An acceptance layer has especially desirable amorphous silica, although the ink absorptivity which mean particle diameter is 2-17 micrometers, and contained at least one sort of pigments chosen from amorphous silica, an alumina, hydrated alumina, aluminosilicate (a zeolite is included), and a hydrotalcite group mineral, and was excellent by this is acquired. Especially, it is JIS. Since the oil absorption according to K5101 is suitable to pigment ink, a pigment's (300ml / 100g or more) is desirable, and as for this pigment, it is desirable to contain this pigment ten to 50% of the weight to all the pigment solid content in an ink absorbing layer.

[0020] There are a wet method and dry process as a process of amorphous silica. the silicon dioxide ( $\text{SiO}_2$ ) with which the silica of a wet method exists so much on the earth - - silica sand is mainly manufactured as a raw material. Amorphous silica can control a physical property by the manufacture approach, and can manufacture amorphous silica with the property according to the purposes of use, such as an object for adsorption separation, catalyst \*\*\*\*\*\*, and a coating, an object for restoration of resin. There are the gel method and a sedimentation method as a process of the amorphous silica of a wet method.

[0021] The amorphous silica of the gel method mixes the sodium silicate and the sulfuric acid which used high grade silica sand as the raw material, and generates a silicic-acid sol. The polymerization of the silicic-acid sol is carried out gradually, it forms a primary particle, and forms and gels still three-dimensions-floc. The amorphous silica from which specific surface area and physical properties, such as pore size, differ can be made by changing the generation condition of a primary particle etc. in this process. What carried out and carried out pulverization of this silica floc to micron size is used.

[0022] The amorphous silica of a sedimentation method is a silica which is made to sediment by stopping growth of secondary floc, and is obtained under the effect of

temperature, coexistence ion, a surfactant, etc. in the reaction condition of the above-mentioned gel method silica. In addition, in order that the amorphous silica of dry process may carry out combustion hydrolysis and may make SiCl<sub>4</sub> in a gaseous phase, it is also called dry process to a wet method. By this approach, it becomes the compact silica which there is no clearance, therefore does not have specific surface area in the interior of a particle.

[0023] As a difference of the process of amorphous silica, the amorphous silica manufactured by the gel method has a small primary particle, and the cohesive force of amorphous silica becomes large and tends to make a comparatively dense aggregated particle. Pore volume is small in order to make a comparatively dense aggregated particle. For this reason, there is an inclination for the direction of the amorphous silica manufactured with the sedimentation method to be excellent in ink receptiveness. The amorphous silica manufactured with the sedimentation method has a large primary particle, and the cohesive force of a silica becomes small and tends to make a comparatively loose aggregated particle. Pore volume is an opening made by condensation of a primary particle, and is controllable description. Generally the amorphous silica manufactured by the gel method forms firm floc mutually compared with the amorphous silica manufactured with the sedimentation method. Contributing to improvement in paint film reinforcement is expected, and such firm flocs have the advantage which raises the pencil note nature which is an element important as office form fitness.

[0024] Although a sedimentation method silica generally has the improvement effectiveness in image quality, surface reinforcement is weak and it is easy to generate paper powder. Although surface reinforcement is strong and paper powder cannot generate the gel method silica easily, a dot configuration may worsen. Both can be used together, and a quality design can be performed so that various printers may be suited.

[0025] Although it has the record fitness as an ink jet record medium when mean particle diameter makes only a less than 2-micrometer pigment contain all over this ink absorbing layer in the ink jet record medium which comes to prepare the ink absorbing layer containing amorphous silica and adhesives on a base material about the ink jet recording method which records on a medium using oily ink or water color ink, there is an inclination for surface reinforcement to be inferior. Moreover, when only the pigment with which mean particle diameter exceeds 17 micrometers all over an ink absorbing layer is made to contain, there is an inclination for the record fitness as an ink jet record medium to be inferior a little. Therefore, 2-17 micrometers (secondary particle diameter) of mean particle diameter of said specific pigment are more preferably adjusted to 2-15 micrometers. Especially, to pigment ink, two or more sorts of things for which amorphous silica is used together are desirable, and it is desirable that the difference of the secondary particle mean particle diameter of two sorts of amorphous silica used together is 2-7 micrometers.

[0026] Other pigments can also be used together. For example, they are the organic pigments of inorganic pigments, such as aluminum silicate, a calcium silicate, a magnesium silicate, colloidal silica, an aluminum hydroxide, a magnesium hydroxide, a calcium carbonate, a kaolin, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc carbonate, a satin white, diatomaceous earth, amorphous silica other than the above, an alumina, and aluminosilicate, a styrene system, acrylic, a urea-resin system,

a melamine resin system, and a benzoguanamine resin system. Floc aggregated particle structure is taken preferably and it divides, and Kamiichi of many forms is carried out industrially, and since an aluminum hydroxide, a magnesium hydroxide, and the amorphous silica except said can choose what was easily equipped with the desired engine performance, they can be used preferably. By using these together, properties, such as note nature with a pencil, are further improvable, for example.

[0027] the purpose which raises the water resisting property of the printing image in oily ink or water color ink -- cation system high molecular compounds, such as cation resin, such as polyethyleneimine system resin, polyamine system resin, polyamide system resin, polyamide epichlorohydrin system resin, a polyamine epichlorohydrin resin, a polyamide polyamine epichlorohydrin resin, poly diaryl amine system resin, diaryl dialkyl quaternary-ammonium-salt acid chloride, and a dicyandiamide condensate, a urea-resin, and melamine resin acid colloid, -- \*\*\*\*\* -- things are made.

[0028] Although especially the content of the cation resin in an ink absorbing layer is not limited, it is desirable to consider as the 3 - 200 weight section to all the pigment 100 weight sections. When the content of cation resin is below 3 weight sections of all pigments, there is a possibility that image repeatability may be inferior. When the content of cation resin exceeds the 200 weight sections of all pigments, there is a possibility that printing drying may be inferior.

[0029] In cation resin, the copolymerization object of a polydiallyldimethylammonium salt and acrylamide is [ as opposed to / especially / pigment ink ] excellent, and effectiveness with about 1 - 10% of the weight of very remarkable combination is acquired by ink absorbing layer total solids.

[0030] Furthermore, a pigment agent, a thickener, a defoaming agent, foam suppressor, a foaming agent, a release agent, a penetrating agent, a wetting agent, a heat gelling agent, lubricant, and other various assistants well-known at the technical field concerned can also be used if needed.

[0031] As a base material of a record medium, although it does not limit, loading materials, such as talc, a kaolin, a baking kaolin, a calcium carbonate, and a silica, can be added if needed to the pulp for paper making, and the stencil paper prepared by the approach usually performed by acidity or neutral paper making can be used suitably. Moreover, as a base material, a dry type or wet nonwoven fabric, a synthetic paper, a film, a laminated paper, etc. can also be used.

[0032] although the amount of coating in an ink absorbing layer is not limited -- about two 1 - 30 g/m -- desirable -- 3 - 20 g/m<sup>2</sup> -- it is 5 - 15 g/m<sup>2</sup> still more preferably. If there are few amounts of coating, although surface reinforcement becomes strong, record image quality may be inferior. Conversely, surface reinforcement may become weak although image quality is good, if there are many amounts of coating.

[0033] As a means to paint an ink absorbing layer, size press, a gate roll, a roll coater, a bar coating machine, an air knife coating machine, a rod blade coating machine, a blade coating machine, etc. can be suitably chosen from the coating means usually used.

[0034] Furthermore, a binder layer and an exfoliation sheet can be prepared in a base material rear face, and it can be processed into a pressure sensitive adhesive sheet. What applied removers, such as a silicone compound and a fluorine compound, to exfoliation stencil paper, such as high density paper like glassine, clay court paper, and a polylaminated paper, can be used for a releasing paper. Moreover, to a binder, the solvent

mold binder of acrylic and a rubber system, an emulsion mold binder, a hot melt mold binder, etc. can be illustrated.

[0035] In the water color ink used in this invention, at least one sort in water-soluble direct dye and water-soluble acid dye is contained as a color, in addition a wetting agent, a color resolvent, antiseptics, an antifungal agent, etc. are contained suitably. As water-soluble direct dye, CI. direct black, CI. direct yellow, CI. direct blue, CI. direct red, etc. are mentioned, and as water-soluble acid dye, although CI. acid black, CI. acid yellow, CI. acid blue, CI. acid red, etc. can be mentioned, it is not necessarily limited to these.

[0036] Moreover, a pigment may be used for the ink used in this invention as a coloring component. Said ink is ink which made the aquosity solution or organic solvent which contains water, isopropyl alcohol, etc. with a dispersant etc. distribute organic or an inorganic pigment particle component. As an organic solvent, for example, methyl alcohol, ethyl alcohol, n-propyl alcohol, The alkyl alcohols of the carbon numbers 1-4, such as isopropyl alcohol, n-butyl alcohol, and isobutyl alcohol, A ketone or ketone alcohol, such as an acetone and diacetone alcohol, Polyalkylene glycols, such as a polyethylene glycol and a polypropylene glycol Ethylene glycol, a polo pyrene glycol, a butylene glycol, Triethylene glycol, thioglycol, hexylene glycol, Alkylene groups, such as a diethylene glycol, 2-6 alkylene glycol Ether, such as amides, such as dimethylformamide, and a tetrahydrofuran, The low-grade alkyl ether of polyhydric alcohol, such as a glycerol, ethylene glycol methyl ether, the diethylene-glycol methyl (ethyl) ether, and the triethylene glycol monomethyl ether, is mentioned. Oily ink can be prepared by these. As an organic pigment, pigments, such as for example, an azo system, a phthalocyanine system, a pel phosphorus system, an isoindolinone system, an imidazolone system, a pyran SURON system, and a thioindigo system, can be illustrated. As an inorganic pigment for example Carbon black, graphite, synthetic ferrous-oxide yellow, a transparency red oxide, titanellow, Pigments, such as a MORIBUTE toe range, a cuprous oxide, cobalt blue, ultramarine blue, C.I.Pigment Yellow (yellow ink), C.I.Pigment Blue (cyanogen ink), and C.I.Pigment Red (Magenta ink), can be illustrated. As said dispersant, various surfactants, the dispersant of low molecular weight, and the dispersant of the resin system which has a hydrophilic functional group and a hydrophobic functional group are used. Moreover, aquosity resin can also be added in order to adjust the viscosity of ink. Blending said pigment and dispersant into a solution, grinding to a detailed particulate material using dispersers, such as a paint shaker and a sand mill, filtering a big and rough particle with the filter of 1.0 micrometers or less of apertures, and considering as pigment ink is usually performed. Although especially the solid content concentration of pigment ink is not limited, it is 0.5 - 30 % of the weight.

[0037]

[Example] Although an example is given to below and this invention is more concretely explained to it, of course, it is not limited to these examples. In addition, number of copies in an example and % show weight section and weight %.

[0038] Specific-surface-area 290m<sup>2</sup>/g manufactured with example 1 sedimentation method, the amorphous silica pigment (trade name: fine seal X-60, Tokuyama make) 100 section with a mean particle diameter of 5.9 micrometers, The 10% water-solution 250 section of silanol-ized polyvinyl alcohol (trade name: R-1130, Kuraray Co., Ltd. make), As cation resin, the polyoxy propyl quarternary-ammonium-salt system cation resin (trade name: SAFUTOMA ST-3300, Mitsubishi Chemical make) 10 section, As a

copolymer which is mainly concerned with vinyl chloride-vinyl acetate The colloid water dispersing element resin (trade name: UCAR WBV-110, made in Union Carbide) 20 section of the copolymer of the vinyl chloride-vinyl acetate-acrylic-acid hydroxypropyl-hydrophilic-property polymer which makes a vinyl chloride a subject is added. After adding water, it considered as the coating liquid for ink absorbing layers of 18% of concentration. After carrying out spreading desiccation using Mayer Bar so that the coverage after drying to the paper of fine quality for basis-weight 80 g/m<sup>2</sup> and Stockigt-sizing-degree 10 seconds may become 10 g/m<sup>2</sup>, supercalender processing was performed and the ink jet record medium was obtained.

[0039] The ink jet record medium was obtained like the example 1 except having made coverage after example 2 desiccation into 7 g/m<sup>2</sup>.

[0040] The ink jet record medium was obtained like the example 1 except having made coverage after example 3 desiccation into 17 g/m<sup>2</sup>.

[0041] The ink jet record medium was obtained like the example 1 except having used the polyamide resin (trade name: poly fix 3000, Showa High Polymer Co., Ltd. make) 10 section as example 4 cation resin.

[0042] The ink jet record medium was obtained like the example 1 except having used specific-surface-area 290m<sup>2</sup>/g manufactured with the sedimentation method as an example 5 amorphous-silica pigment, the amorphous silica pigment (trade name: fine seal X-60, Tokuyama make) 50 section with a mean particle diameter of 5.9 micrometers, and specific-surface-area 400m<sup>2</sup>/g manufactured by the gel method and the amorphous silica pigment (trade name: Carplex BS304N, Shionogi& Co., Ltd. make) 50 section with a mean particle diameter of 9.3 micrometers.

[0043] The ink jet record medium was obtained like the example 5 except having used the polydiallyldimethylammoniumchloride cation resin (trade name: uni-sense CP- 103, product made from SENKA) 10 section of molecular weight 100,000 [ about ] as example 6 cation resin.

[0044] the ink jet record medium was obtained like the example 6 except having used the vinyl chloride-vinyl acetate-ethylene copolymer (trade name: -- SUMIKA flex time 801, Sumitomo Chemical Co., Ltd. make, water dispersing element [ of 0.7 micrometers ], and viscosity in 50% -- 700 - 2500 mPa·s) 20 section as a copolymer which is mainly concerned with example 7 vinyl-chloride-vinyl acetate.

[0045] The ink jet record medium was obtained like the example 1 except having not blended the copolymer which is mainly concerned with the vinyl chloride-vinyl acetate of the coating liquid for example of comparison 1 ink absorbing layers.

[0046] The ink jet record medium was obtained like the example 1 except having used specific-surface-area 290m<sup>2</sup>/g manufactured with the sedimentation method as an example of comparison 2 amorphous-silica pigment, and the amorphous silica pigment (trade name: fine seal X-20, Tokuyama make) 100 section with a mean particle diameter of 1.9 micrometers.

[0047] The ink jet record medium was obtained like the example 1 except having used specific-surface-area 195m<sup>2</sup>/g manufactured with example of comparison 3 sedimentation method, and the amorphous silica pigment (trade name: nip seal VN3, Japanese silica industrial company make) 100 section with a mean particle diameter of 18 micrometers.

[0048] The ink jet record medium was obtained like the example 1 except having used

the vinyl acetate copolymer (trade name: YODOZORU CE-58, product made from Japanese ENUESUSHI) 20 section instead of the copolymer which is mainly concerned with example of comparison 4 vinyl-chloride-vinyl acetate.

[0049] The ink jet record medium was obtained like the example 1 except having used the vinyl acetate-ethylene copolymer (trade name: SUMIKA flex time 473, Sumitomo Chemical Co., Ltd. make) 20 section instead of the copolymer which is mainly concerned with example of comparison 5 vinyl-chloride-vinyl acetate.

[0050] The ink jet record medium was obtained like the example 1 except having used the vinyl acetate-ethylene-acrylic copolymer (trade name: SUMIKA flex time 940, Sumitomo Chemical Co., Ltd. make) 20 section instead of the copolymer which is mainly concerned with example of comparison 6 vinyl-chloride-vinyl acetate.

[0051] The following evaluation trial was performed about the ink jet record medium created in the [quality comparison test] examples 1-7 and the examples 1-6 of a comparison. Those results are shown in Table 1.

[0052] Evaluation 1 [image repeatability]

Concentration gradation was printed with the recording density of 1440dpi using ink jet printer PM-770C of Seiko Epson aquosity color ink (from 100% printing to 90%, 80%, 70% ... 20%, and 10%), and linearity with printing concentration (measured value according record concentration to the Macbeth optical-density meter) was made into the scale of image repeatability.

(Valuation basis)

O : -- \*\*: which is excellent in linearity -- a little inferior x: -- practical use is impossible  
-- [0053] Evaluation 2 [image repeatability]

The printing pattern of concentration gradation was incorporated by the color hand copy using color facsimile UX-E1CL of the oily pigment ink by Sharp Corp., concentration gradation was printed (from 100% printing to 90%, 80%, 70% ... 20%, and 10%), and linearity with printing concentration (measured value according record concentration to the Macbeth optical-density meter) was made into the scale of image repeatability.

(Valuation basis)

O : -- \*\*: which is excellent in linearity -- a little inferior x: -- practical use is impossible  
-- [0054] Evaluation 3 [printing drying]

the product made from Hewlett Packard -- solid printing was performed using ink jet printer DeskJet560J (aquosity color ink), viewing estimated the dryness of the part and time amount until it dries was made into the printing drying scale.

(Valuation basis)

O : it is good (time amount until it dries is 2 or less seconds).

\*\*: It is a little inferior (2 - 10 seconds).

x: Practical use is impossible (10 seconds is exceeded).

[0055] Evaluation 4 [surface reinforcement]

A friction child's mass was set to 400g in the friction tester II form (\*\*\*\* form) of a publication at JIS-L -0849, on the friction child tip and the test piece base, the ink absorbing layer was made to counter, the test piece was attached, both-way friction of between 100mm of test pieces was carried out 10 times, and it evaluated from the existence of omission on the front face of an ink absorbing layer, and extent of generating of paper powder.

(Valuation basis)

O : -- O: without surface omission and generating of paper powder -- omission of x:front face where omission of \*\*:front face where generating of paper powder is accepted slightly, and generating of paper powder are accepted, and generating of paper powder are remarkable, and practical use is impossible.

[0056] Evaluation 5 [a water resisting property]

Seiko Epson aquosity color ink (yellow ink contains an azo system color.) Magenta ink contains an azo system color. Cyanogen ink performs solid printing using ink jet printer PM-770C containing a phthalocyanine system blue color, and will leave it on the 1st. Water will be dropped at the printing object after neglect for one day. Viewing estimated the blot of the ink of the printing section for the printing object after the air dried.

(Valuation basis)

O : -- a blot of ink -- there is nothing -- fitness \*\*: -- a little inferior x:practical use is impossible.

[0057] Evaluation 6 [a water resisting property]

A solid printing pattern is incorporated by the color hand copy using color facsimile UX-E1CL of the oily pigment ink by Sharp Corp., solid printing is performed, and water is dropped at a printing object immediately after printing. Viewing estimated the blot of the ink of the printing section for the printing object after the air dried.

(Valuation basis)

O : -- a blot of ink -- there is nothing -- fitness \*\*: -- a little inferior x:practical use is impossible -- [0058]

[Table 1]

[0059] Table 1 shows that each example which blended the copolymer which is mainly concerned with vinyl chloride-vinyl acetate is excellent in a water resisting property much more as compared with the example of a comparison (examples 1, 4, 5, and 6 of a comparison) which is not used. Moreover, it turns out that surface reinforcement falls that it is less than 2 micrometers (example 2 of a comparison), and mean particle diameter has the pigment to be used in the inclination which is inferior in record fitness in it being only the pigment with which mean particle diameter exceeds 17 micrometers. Next, the result of having advanced examination further about pigment ink is shown.

[0060] 310ml of oil absorbency, 100g manufactured by the gel method as an example 8 amorphous-silica pigment, 170ml of oil absorbency, 100g manufactured by the

amorphous silica pigment (trade name: silo jet P405, product made from GRACE Davison) 50 section with a mean particle diameter of 3.5 micrometers (the Coulter counter method), and the gel method, an amorphous silica pigment (trade name: -- Carplex BS -- 304 N) with a mean particle diameter of 9.3 micrometers (the Coulter counter method) The 50 by Shionogi & Co., Ltd. section, the 10% water-solution 250 section of silanol-ized polyvinyl alcohol (trade name: R-1130, Kuraray Co., Ltd. make), as cation resin -- the copolymer (trade name: -- KZ76K --) of molecular-weight about 500,000 polydiallyldimethylammoniumchloride, and acrylamide The product made from SENKA, 22% 45 sections of solid content concentration, and the colloid water dispersing element resin (trade name: UCAR WBV-110, made in Union Carbide) 20 section of the copolymer of a vinyl chloride-vinyl acetate-acrylic-acid hydroxypropyl-hydrophilic-property polymer are added. After adding water, it considered as the coating liquid for ink absorbing layers of 18% of concentration. After carrying out spreading desiccation using Mayer Bar so that the coverage after drying in the high-quality pasteboard for basis-weight 140 g/m<sup>2</sup> and Stockigt-sizing-degree 15 seconds may become 10 g/m<sup>2</sup>, supercalender processing was performed and the ink jet record medium was obtained.

[0061] 310ml of oil absorbency, 100g manufactured by the gel method as an example 9 amorphous-silica pigment, 170ml of oil absorbency, 100g manufactured by the amorphous silica pigment (trade name: silo jet P409, product made from GRACE Davison) 10 section with a mean particle diameter of 5.5 micrometers (the Coulter counter method), and the gel method, The ink jet record medium was obtained like the example 8 except having used the amorphous silica pigment (trade name: Carplex BS304N, Shionogi & Co., Ltd. make) 90 section with a mean particle diameter of 9.3 micrometers (the Coulter counter method).

[0062] the ink jet record medium was obtained like the example 8 except having used the vinyl chloride-vinyl acetate-ethylene copolymer (trade name: -- SUMIKA flex time 801, Sumitomo Chemical Co., Ltd. make, water dispersing element [ of 0.7 micrometers ], and viscosity in 50% -- 700 - 2500 mPa·s) 20 section as a copolymer which is mainly concerned with example 10 vinyl-chloride-vinyl acetate.

[0063] The ink jet record medium was obtained like the example 8 except having used the copolymer (trade name: KZ76K, product [ made from SENKA ], 22% of solid content concentration) 10 section of molecular-weight about 500,000 polydiallyldimethylammoniumchloride, and acrylamide as example 11 cation resin.

[0064] The ink jet record medium was obtained like the example 8 except having used the copolymer (trade name-AS-J-81, Nittobo Co., Ltd. make, 25% of solid content concentration) 10 section of molecular-weight about 150,000 polydiallyldimethylammoniumchloride, and acrylamide as example 12 cation resin.

[0065] 310ml of oil absorbency, 100g manufactured by the gel method as an example 13 amorphous-silica pigment, 170ml of oil absorbency, 100g manufactured by the amorphous silica pigment (trade name: silo jet P407, product made from GRACE Davison) 5 section with a mean particle diameter of 4.5 micrometers (the Coulter counter method), and the gel method, The ink jet record medium was obtained like the example 8 except having used the amorphous silica pigment (trade name: Carplex BS304N, Shionogi & Co., Ltd. make) 90 section with a mean particle diameter of 9.3 micrometers (the Coulter counter method).

[0066] The ink jet record medium was obtained like the example 8 except having used

310ml of oil absorbency manufactured by the gel method as an example of reference 1 amorphous-silica pigment, 100g, and the amorphous silica pigment (trade name: silo jet P407, product made from GRACE Davison) 100 section with a mean particle diameter of 4.5 micrometers (the Coulter counter method).

[0067] The ink jet record medium was obtained like the example 8 except having used the copolymer (trade name: KZ76K, product [ made from SENKA ], 22% of solid content concentration) 80 section of molecular-weight about 500,000 polydiallyldimethylammoniumchloride, and acrylamide as example of reference 2 cation resin. [0068] The 10% water-solution 600 section of example of reference 3 silanol-ized polyvinyl alcohol (trade name: R-1130, Kuraray Co., Ltd. make), as cation resin -- the copolymer (trade name: -- KZ76K --) of molecular-weight about 500,000 polydiallyldimethylammoniumchloride, and acrylamide The product made from SENKA, 22% 45 sections of solid content concentration, The ink jet record medium was obtained like the example 8 except having used the colloid water dispersing element resin (trade name: UCAR WBV-110, made in Union Carbide) 80 section of the copolymer of a vinyl chloride-vinyl acetate-acrylic-acid hydroxypropyl-hydrophilic-property polymer.

[0069] The ink jet record medium was obtained like the example 8 except having not blended the copolymer of molecular-weight about 500,000 polydiallyldimethylammoniumchloride, and acrylamide as example of reference 4 cation resin.

[0070] The following evaluation trial was performed about the ink jet record medium created in the [quality comparison test] examples 8-13 and the examples 1-4 of reference. Those results are shown in Table 2.

[0071] Evaluation 7 [record concentration]

Ink jet printer of King Jim watercolor pigment ink Solid printing of cyanogen monochrome was performed in recommended mode (360x720dpi) using TEPURA JETJCR770, and the record concentration of the solid Records Department was measured with the Macbeth densimeter (made in Macbeth, trade name:RD-914 mold) 1 hour after printing. The filter used the red filter.

[0072] Evaluation 8 [image repeatability]

The printing pattern of concentration gradation was incorporated by the color hand copy using color facsimile UX-E1CL of the oily pigment ink by Sharp Corp., concentration gradation was printed, and linearity of the rate of printing area and printing concentration was made into the scale of image repeatability.

(Valuation basis)

O : -- \*\*: which is excellent in linearity -- a little inferior x: -- practical use is impossible  
-- [0073] Evaluation 9 [printing drying]

Ink jet printer NOVA made from ENCAD JET Solid printing of 200% of rates of color overlapping in GO ink (watercolor pigment ink) was performed using Pro, viewing estimated the dryness of the part and time amount until it dries was made into the printing drying scale.

(Valuation basis)

O : it is good (time amount until it dries is 2 or less seconds).

\*\*: It is a little inferior (2 - 10 seconds).

x: Practical use is impossible (10 seconds is exceeded).

[0074] Evaluation 10 [surface reinforcement]

A friction child's mass was set to 400g in the friction tester II form (\*\*\*\* form) of a publication at JIS-L -0849, on the friction child tip and the test piece base, the ink absorbing layer was made to counter, the test piece was attached, both-way friction of between 100mm of test pieces was carried out 10 times, and it evaluated from the existence of omission on the front face of an ink absorbing layer, and extent of generating of paper powder.

(Valuation basis)

O : -- O: without surface omission and generating of paper powder -- omission of x:front face where omission of \*\*:front face where generating of paper powder is accepted slightly, and generating of paper powder are accepted, and generating of paper powder are remarkable, and practical use is impossible -- [0075] Evaluation 11 [a water resisting property]

Ink jet printer of King Jim watercolor pigment ink Using TEPURA JETJCR770, in quick mode (360x360dpi) color overlapping, solid printing is performed and it will be left for one day. Water was dropped at the printing object after neglect on the 1st, it rubbed with tissue paper (product made from NEPIA, Inc.) with the pressure of about 500 gf/cm<sup>2</sup> from the top, and viewing estimated the blur of a printing object.

(Valuation basis)

O : -- the blur of the Records Department -- there is nothing -- fitness \*\*: -- the practical use improper level [0076] which becomes blurred a little and on which it x: becomes blurred and a color disappears

[Table 2]

[0077] From Table 2, it is JIS. When the loadings of a pigment (300ml / 100g or more) increase [ the oil absorption according to K5101 ], it turns out that record concentration becomes high in pigment ink (an example 8 is compared with examples 9 and 13). However, when the loadings of a pigment (300ml / 100g or more) have too much oil absorption, it also turns out that it is in the inclination for a water resisting property to be inferior (example 1 of reference). Therefore, 10 - 50% of the weight of the pigment in an ink absorbing layer has [ the loadings of a pigment (300ml / 100g or more) ] desirable oil absorption. Moreover, it also turns out that what used together the amorphous silica whose difference of secondary particle diameter is 2-7 micrometers is excellent in pigment ink (comparison of examples 8-13 and the example 1 of reference). Furthermore, using the copolymer of a polydiallyldimethylammonium salt and acrylamide as cation resin also turns out to excel in pigment ink (comparison of examples 8-13 and the

example 4 of reference). When blending the copolymer of a polydiallyldimethylammonium salt and acrylamide, 1 - 10% of the weight of combination is suitable to ink absorbing layer total solids, and when 10 % of the weight is exceeded, it is in the inclination inferior to printing drying or a water resisting property (comparison of examples 8-13 and the example 2 of reference).

[0078]

[Effect of the Invention] Thus, the ink jet record medium obtained in the example of this invention is an ink jet record medium which has functions, such as the image repeatability as an ink jet record medium, and printing drying, and was excellent in the water resisting property especially as shelf life.